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SEASONAL CHEMICAL EVOLUTION OF THE ALGA *CYSTOSEIRA ELEGANS*

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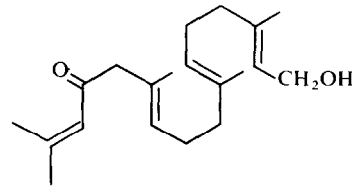
Key Word Index—*Cystoseira elegans*; Cystoseiraceae; Phaeophyceae; eleganolone; acyclic diterpenoids.

Abstract—Among the Mediterranean algae belonging to the family Cystoseiraceae analysed for diterpenic compounds, only *Cystoseira elegans* contains eleganolone, epoxy-eleganolone and elegandiol, as does the Atlantic alga *Bifurcaria bifurcata*. Surprisingly, for the seasonal *Cystoseira elegans*, these compounds are present only at the beginning of growth of the alga during Spring and they disappear in the Summer yielding important seasonal variation data for diterpenoids, and also for sterols, alginic acid, mannitol and cellulose.

INTRODUCTION

The brown alga *Cystoseira elgans* is a very typical plant of the Catalan Mediterranean coast near Banyuls sur Mer. In Autumn the alga is at rest, branches and leaves appearing at the beginning of Spring and disappearing in August. From April to July, we have observed a seasonal chemical variation of alginic acid, mannitol, cellulose and sterols, these compounds being analysed by previously described methods. The acyclic diterpenoids already identified from *Cystoseira elegans*, and from another Cystoseiraceae *Bifurcaria bifurcata* [1–3], eleganolone (**1**), the related epoxy-eleganolone (**2**) and elegandiol (**3**), are also analysed. An analytical method utilizing IR spectrometry and GLC has been developed for a rapid and easy identification of these compounds in extracts of algae.



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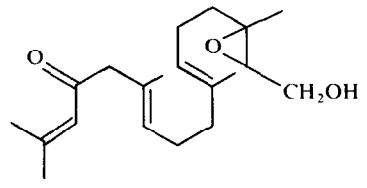

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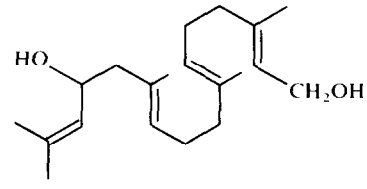

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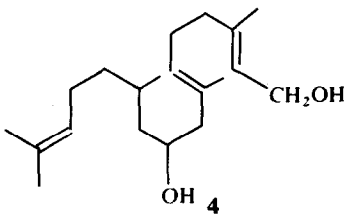
RESULTS AND DISCUSSION

Cystoseira elegans is the only Mediterranean *Cystoseira* species analysed which was found to contain the diterpenoid compounds **1**, **2** and **3** (Table 1). These compounds were also present in *Bifurcaria bifurcata*. *B. bifurcata*, an Atlantic, perennial Cystoseiraceae, showed a seasonal variation of eleganolone (**1**) from January (1.5% dry wt) to July (3% dry wt). For *C. elegans*, which is a

Table 1. Mediterranean *Cystoseira* species analysed which did not contain the diterpenic compounds 1, 2 and 3

Species	Date	Location	Ether extract, % of dry wt
Cystoseira mediterranea	February 1980	Banyuls sur Mer	3.06
C. fimbriata	July 1978	—	0.28
C. fimbriata	May 1979	—	0.18
C. zosteroides	March 1979	Roche Torreilles (−25 m)	2.96
*C. crinita**	March 1980	Les Issambes	0.94
C. crinita,	March 1980	Collioure	1.24
C. crinita	March 1980	Banyuls sur Mer	1.26
C. crinita	April 1980	Banyuls sur Mer	1.16
C. barbata	March 1980	Sigean	1.49
C. barbata	May 1980	Sigean	1.12
C. discors	March 1980	Collioure	0.70
C. caespitosa	February 1980	Banyuls sur Mer	2.11

* Crinitol 4 has been identified from the Sicilian *C. crinita* [1].



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seasonal plant, the diterpenoid compounds are present in the Spring during the appearance of the alga and the beginning of growth. They are absent before the alga disappears in the Summer (Table 2). To examine the chemical evolution of the alga we also analysed carbohydrates and sterols during the same period and did not observe a very significant variation from April to June, whereas in July the alga is quite different (Table 2). At this time, just before the alga disappears, sterols and carbohydrates are stored. This is a general and interesting point that most secondary metabolite synthesis in micro-organisms occurs in the later stages of growth, i.e. just before and during the resting phase. *Cystoseira elegans* is unusual in that synthesis of diterpenoid compounds only occurs during growth. This is what would be expected if the components are stored in the new tissues as feeding deterrents. An important fact, however, is if stored, they must decompose when the plant reaches a certain age.

Table 2. Seasonal variation of constituents of *Cystoseira elegans* analysed during 1978

	April	May	June	July
Ether extract	2.13*	1.94	1.81	1.72
Acyclic diterpenes				
1	0.6	0.3	—	—
2	0.1	0.1	—	—
3	0.1	0.05	—	—
Sterols				
Fucosterol	0.03	0.02	0.02	0.09
Cholesterol	tr.	tr.	tr.	0.01
Carbohydrates				
Mannitol	7	6	6	12
Alginic acid	27	26	30	26
Cellulose	8	6	8	6

*Expressed as % of dry wt of alga.

EXPERIMENTAL

Extraction. Freeze-dried algae (5 g) were extracted with Et_2O (3 × 50 ml, 3 × 3 hr, 20°).

Diterpenoid analysis. The very typical IR spectrum of 1 was very similar to that of mesityl oxide which has the *S-cis* conformation ($\nu_{C=C}$ 1620 cm^{-1} stronger than $\nu_{C=O}$ 1680 cm^{-1}) and allowed the identification of 1 and related compounds in crude extracts. GLC on a glass column of the MO-TMS derivatives had previously led to a very good separation of diterpenoid compounds [2]. Therefore similar selectivity can be obtained by injecting the crude extracts in CS_2 onto a 5% OV-1 column. Programming at the rate of 2° min from 200° to 300° gives methylene units (MU) of 21.42, 22.34 and 23.01 respectively for 2, 3 and 1.

Authentic 1 was obtained from *Cystoseira elegans* or *Bifurcaria bifurcata* extracts by Si gel chromatography. Compound 2 from *B. bifurcata* was purified by prep. HPLC. Compound 3 was prepared by $LiAlH_4$ reduction of 1 [2, 3]. Sterols, cellulose, mannitol and alginic acid were analysed by previously described methods [4, 5].

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